Year: 2010

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DOI: https://doi.org/10.1007/s12274-010-0062-0

Originally published at:
Stojanovic, A; Artus, G R J; Seeger, S (2010). Micropatterning of superhydrophobic silicone nanofilaments by a near-ultraviolet Nd:YAG laser. Nano Research, 3(12):889-894.
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Micropatterning of Superhydrophobic Silicone Nanofilaments by Near-ultraviolet Nd:YAG Laser

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ABSTRACT

We demonstrate that a recently developed coating comprised of superhydrophobic silicone nanofilaments can be selectively functionalized to yield well defined micrometer scale patterns of contrasting wettabilites (superhydrophobic/hydrophilic and amphiphobic/amphiphilic). Nanofilament ablation have been performed by near-ultraviolet (UV) laser at 355 nm and with repetition rate of 10 kHz. This is a highly promising approach for open channel microfluidics and micro array analysis due to its simplicity, chemical and environmental stability of coating and low coast.

KEYWORDS

Superhydrophobic, UV laser ablation, wettability, open channels

Introduction

Artificial superhydrophobic surfaces have generated a lot of attention in last decade due to their significant potential for industrial and scientific applications. Ever since Barthlott and Neinhuis discovered how the chemical and structural nature of the lotus leaf surface provided its strong water repellent properties [1], a variety of materials and techniques have been developed to mimic that effect [2-6]. While patterning extremely hydrophilic and superhydrophobic domains on same surface has only emerged in recent years and still remain a challenge. Structured surfaces that exhibit lateral patterns of varying wettabilty could be produced by different techniques, such as microcontact printing [7], photolithography [8-9], deep reactive ion etching [10], plasma etching as well as using different chemical methods [11] or combining two or more of the technique listed above [12]. Laser-assisted

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processes are of particular interest to produce devices for microfluidics, bioanalytics, bio-reactors and micro-optics [13-14]. Laser micromachining, being a non-contact process, does not have the problems of mechanical damage and tool wear. Pattern configuration and channel size can be faithfully reproduced and exactly created according to various necessities with high geometric flexibility. Also the substrates do not have to be additionally pre- and/or post-treated.

Systems displaying saptially controlled wettability can provide many benefits, such as fewer reagents, faster operations, lower cost and increased sensitivity. Obvious prerequisites for such lab-on-a-chip devices are appropriate compartments for the confinement of very small amounts of liquids. These "microcompartments" should have some basic properties: they should have a well defined geometry in order to measure the precise amount of liquid contained; they should be able to confine variable amounts of liquid; and they should be accessible in such a way that one can add and extract liquid in a convenient manner.

In the present study, a UV laser has been used to create systems with a high wettability contrast. Additionally we demonstrated the production of lens-shaped droplets composed of two immiscible liquids on an amphiphobic surface and propose possible applications of such systems.

Results and discussion

Superhydrophobic silicone nanofilaments represent excellent substrates for the production of the micron-scale regions of contrasting wettabilites. Initially, they were fabricated using a versatile and inexpensive technique by which a dense layer of silicone nanofilaments was grown onto various substrates [15, 16]. For this purpose optically transparent substrates were coated such as glass and quartz. The combination of the hydrophobicity of the silicone and the surface topography formed by the nanofilaments renders the coated materials superhydrophobic. The obtained coating consists of poly-methylsilsequioxane nanofilaments and can be applied in the gas phase or a solvent phase reaction. It is fully transparent in the visible range and exhibits an exceptional chemical and environmental stability [17, 18].

Contrasting wettabilities domains (e.g. superhydrophobic /-philic and amphiphobic/-philic) were produced by exposing different regions of the substrate to a UV laser causing ablation of the silicone nanofilament coating. Material removal by laser ablation, which is both photochemical and photothermal, depends upon many parameters such as the laser beam characteristics and ambient conditions. Russo *et al.* [19], reported that for a nanosecond laser pulse with irradiances less than 10^8 W/cm^2, the dominant mechanism is thermal vaporization; the temperature of the solid surface increases, and a well defined phase transition occurs, from solid to liquid, liquid to vapor and vapor to plasma. The laser processing usually uses a UV laser to ablate insulating materials due to its small spot size and small heat affect zone (HAZ) [20].

Figure 1 (a) shows representative SEM images of the structure of the silicone nanofilaments which are irregularly bent and hooked, roughly 10-30 nm in diameter and anything from 50 nm to few micrometers in length. In figure 1 (b) a coated quartz substrate with laser ablated parallel lines around 1 μm wide and with a distance approximately 15 μm in between is shown.

In the case of quartz slides the lines and channels are produced by repeating scanning irradiation up to ten times while in the case of glass samples the same shapes are produced by a single scan. This may be explained by the fact that quartz is totally transparent at the used wavelength, while the glass is highly absorptive. Absorbed energy generates heat causing the nanofilaments to be

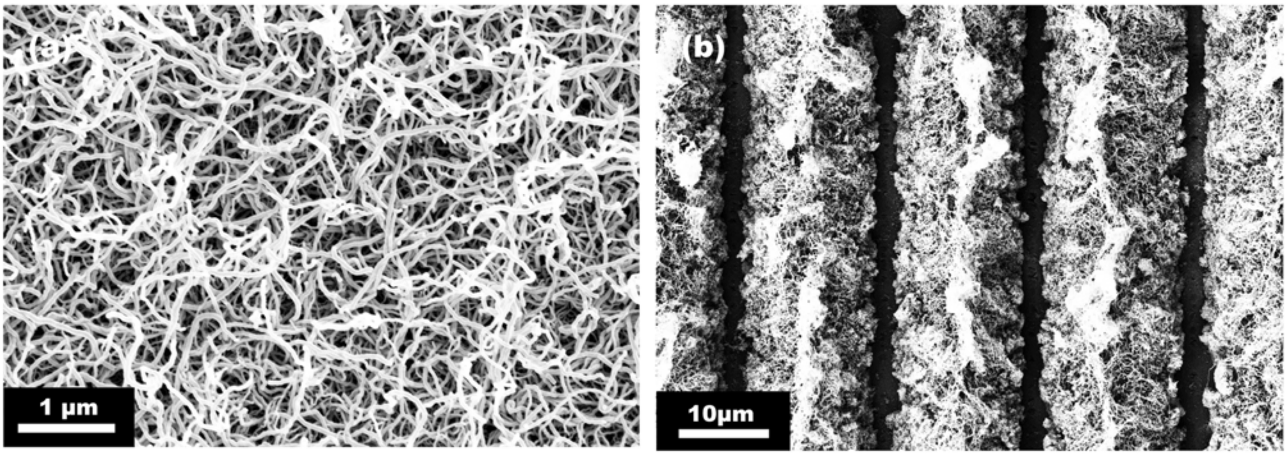


Figure 1. Scanning electron micrographs: (a) topography of silicone nanofilamets coating; (b) laser ablated lines 1-1.5 μm wide with distance around 10 μm in between.

removed faster and a certain amount of the solidified molten material remains in cutting kerfs due to thermal processes characteristic for nanosecond pulse laser ablation [21, 22].

Using this technique, micron scale hydrophilic structures were created on superhydrophobic silicone nanofilaments substrate. Patterned substrates were dipped in aqueous fluorescent dye solution (concentration of fluorescein was [10^{-9}] mol/L) for one hour and immediately observed without rinsing by fluorescence microscopy (Nikon-TE2000-S, Inverted Floresence microscope). Dye solution applied to the laser patterned surface spreads only on the ablated hydrophilic regions and does not penetrate the superhydrophobic background. Figure 2 (a) shows the dye absorbed to hydrophilic channels (20 μm wide) on a superhydrophobic background visualized by inverted fluorescence microscope, while on Fig. 2 (c) a representative SEM image of the laser patterned channels is shown.

There was also a possibility to make different shapes with laser such as circles, squares and ellipses. They are produced by irradiating the concentric circles, or ellipses or squares until the desired size is reached. Substrate patterned with various shapes is presented in Fig. 2 (b). The hydrophilic domains are visualized using the fluorescent dye as with the channels in Fig. 2 (a) and representative SEM images are shown in Fig. 2 (d and e).

A droplet on a surface with patterned, superhydrophobic and completely wetting domains prefers to sit on top on hydrophilic domains. This usually happens even if a droplet is initially pipetted onto a hydrophobic domain, since the droplet dispensed by pipetting always has a some kinetic energy and the friction between the surface and the droplet is extremely small [23]. Droplets of aqueous solution remain attached to hydrophilic domains even when the sample was turned upside down. The ability to confine droplets to desired areas on a substrate facilitates their transport and specific analysis. Figure 3 shows colored water droplets confined on irradiated hydrophilic circles (radius 300 μm) while the sliding angle of the rest of the surface is 3°. The radius of 300 μm is achieved irradiating concentric circles with a distance less then 1 μm in between Changing ablation speed from 2, 7 μm/s to 27 μm/s caused no significant changes in the SEM images of ablated lines and also no difference in the wetting properties of ablated substrates observed (see Fig. S-1 in the Electronic Supplementary Material (ESM). Contact angle of irradiated circles was measured placing 5 μl water droplets on irradiated domains and average value was 58°.

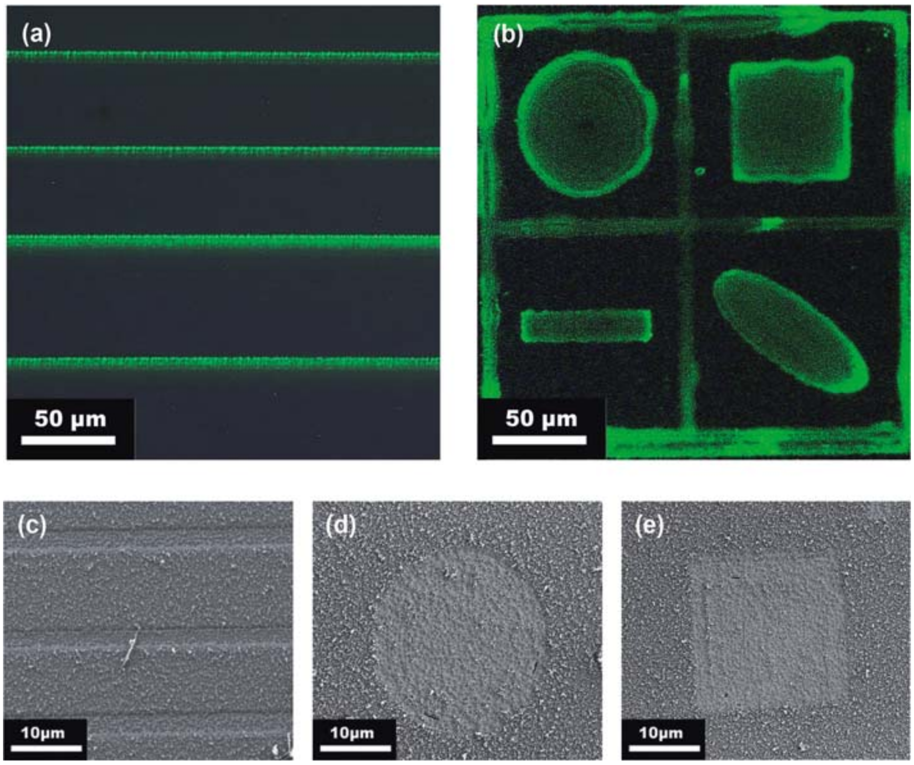


Figure 2. Production of various hydrophilic patches: (a and b) florescent dye solution absorbed on hydrophilic regions (c, d and e) SEM images of various laser ablated regions

Coating of silicone nanofilaments without further modification is ideally non wetting for water; however, they are almost completely wet by hexadecane and other non-polar solvents. If the nanofilaments are exposed to oxygen plasma to generate reactive OH-groups and refunctionalized with a fluorinated molecule such as 1H,1H,2H,2H-perfluorooctyltrichlorosilane (PFOTS), the coating becomes non wetting for both polar and non polar liquids while the surface topography remains the same. After treatment with PFOTS, water and hexadecane exhibit contact angles of 168 ± 2° and 140 ± 5°, respectively [24].

Fluorinated samples were irradiated in a specific pattern to produce features that could comprise two different immiscible liquids and protect aqueous droplets from fast evaporation as shown in Fig. 4(a).

A water droplet was placed on the central small irradiated circle and oil was deposited on the surrounding ring shaped irradiated surface.

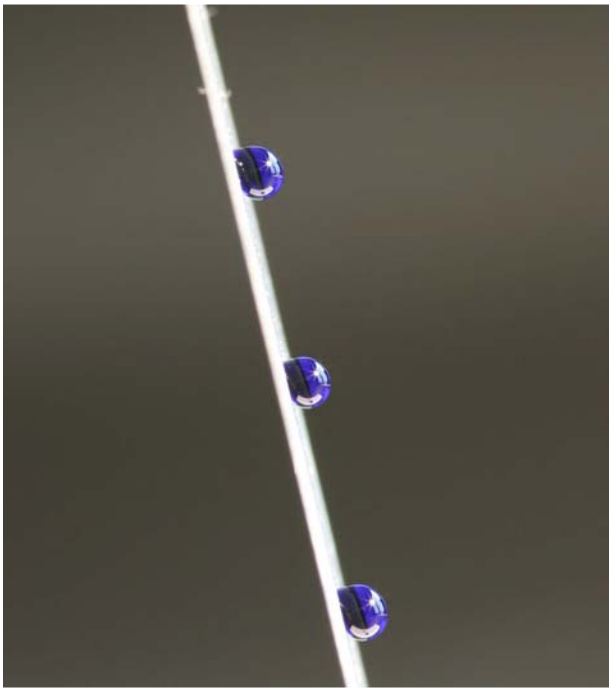
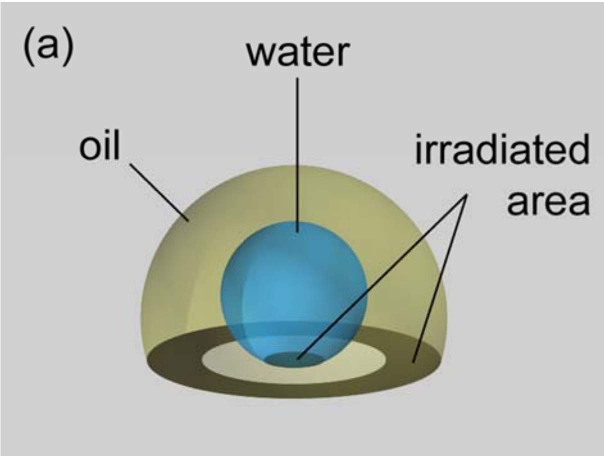


Figure 3. Colored water droplets pinned on hydrophilic domains even if substrate is turned upside-down while sliding angle of the rest of the surface is just 3°.

Upon increasing the volume of the oily

liquids by syringe the water drop remained trapped inside the oil drop in defined position preventing its evaporation. Figure 4(b) shows a colored water droplet inside a larger hexane droplet. The diameter of central circle was 200 μm the distance between irradiated areas 300 μm and outer diameter is 1 mm. Of course this value can vary depending on the volume of the aqueous droplets of interest.



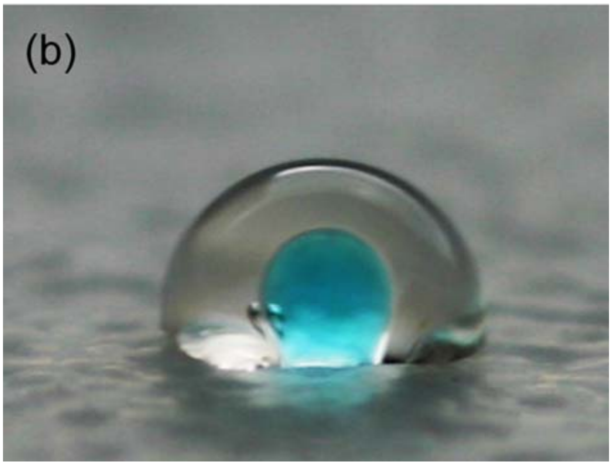


Figure 4. Systems of two immiscible liquids with suppressed evaporation and accurate position of aqueous liquid: (a) schematic illustration of patterns irradiated by laser (b) photograph made of a small water droplet contained within hexadecane

By touching the water droplet with a syringe needle is possible to displace it from the surface forcing the aqueous drop starts to float in the "oil chamber" as it is shown in Fig. 5. This opens the possibility of adding and/or extracting aqueous reactants from the oil droplet which stayed fixed on the irradiated (amphiphilic) domains. Features such as this could be used as "microvessels" where small volumes of aqueous reactants can be kept and analyzed for long periods of time whilst being protected from evaporation. The exceptional chemical and environmental stability of silicone nanofilaments opens the possibility to operate with various polar and non polar liquids.

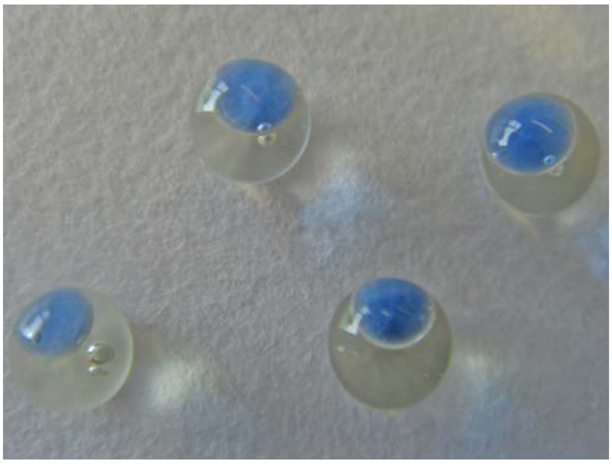


Figure 5 Oil "microvessels" with colored water droplets inside

Concluding remarks

We have presented a simple method of patterning one-dimensional superhydrophobic silicone nanofilaments on surfaces. The straightforward procedure enables the creation of superhydrophilic/superoleophilic patches of arbitrary shape, with micron precision, embedded into superhydrophobic or amphiphobic background. The size of the hydrophilic domains can vary from 1.5 microns to few millimeters and open channel microfludic devices are one manifest application. Patterned amphiphilic circles composed of two different liquids provide an interesting platform for storage of rapidly evaporating liquids and controlled mixing studies. Further, ring shaped features could be used for accurate deposition of aqueous liquids with suppressed evaporation. The fact that substrates are transparent opens the possibility to investigate confined droplets underneath the substrate with several spectroscopic methods. Different microarrays can be performed quickly and in large numbers in a parallel mode of operation, enabling the collection of large volumes of data more rapidly only from one patterned substrate.

Methods

Glass coverslips (26 mm x 76 mm x 1 mm) were purchased from Menzel Gläser (Germany). Quartz slides (26 mm x 76 mm x 0.5 mm) were purchased from SPI supplies (USA). Prior to coating for 5 min at 100 W power generator oxygen plasma Femto from Diener (Nagold, Germany) was used to generate OH-groups on substrate surface.

Substrates were coated in a custom built reaction chamber (volume~ 700ml) at room temperature. 250ml of toluene (Acros, extra dry) was used as solvent. The water content of the solvent was adjusted inside the reaction chamber by flushing the chamber with dry or humidified nitrogen. A coulometric Karl-Fisher Titrator DL32 (Metter Toledo) was used to determine the final water content. Trichloromethylsilane (ABCR, Germany) was introduced into reaction chamber through a septum with a µl syringe (Hamilton). The reaction mixture was stirred with a remote controlled magnetic stirrer (H+P Labortechnik) at 240 rpm. Substrates remained in the reaction chamber overnight. Details on coating procedure can be found in previous publications [16- 18].

After coating the substrates typically exhibit static contact angles of around 160 ± 2^0 and sliding angles of 15 ± 4^0 for 10 µl water drops.

To add oleophobic functionality to the coating, the coated samples were first activated in oxygen plasma machine "Femto" from Diener electronic (Nagold, Germany) at 100 W generator powers for 5 min. Functionalization of the activated substrates was subsequently achieved by placing the substrate in 1 mmol solution of 1H,1H,2H,2H-perfluorooctyltrichlorosilane (PFOTS) in anhydrous toluene (ACROS) overnight.

Annealing was performed in a drying oven (Heraeus, Switzerland) at 200 ^{0}C under ambient atmosphere for four hours. After annealing the contact angle and sliding angle values were improved by roughly 4-6° and 10-15°, respectively.

Contact angle measurements were performed on a Contact Angle System OCA and included software (DataPhysics, Germany). For static contact angle measurements, digital drop shape analysis was performed on a 10 µl sessile drop of deionised water using Laplace Young fitting routine. Sliding angles were measured with the help of a home built tilting table, also on a 10 µl drop. Reported values were an average of minimum of three measurements taken on prepared set of samples. All measurements were performed at ambient conditions.

Electron Microscopy was performed with a SUPRA 50VP (Zeiss, Germany). Samples were coated with 7 nm platinum and analyzed at 5 kV using SE2 detector.

UV laser ablation were performed using commercial setup for microdissection (mmi CellCut Plus System) consist of a inverted microscope (Nikon, Eclipse TE2000-S) with motorized stage, an electronically controlled passive switched tripled Nd:YAG laser at 355 nm wavelength, requisite laser beam delivery and transfer optics. Pulse width was 0.4 nm, frequency 10 kHz and average power 6.6 mW.

Acknowledgements

We thank the Zentrum Mikroskopie & Bildanalyse of the University of Zürich for the opportunity to use their facilities and Swiss National Foundation (SNF) for financial support.

Electronic Supplementary Material: Supplementary material (Fig. S-1 (a) in the ESM presents lines ablated using different ablation time namely different speed of moving sample holder while laser is fixed. Speed can vary from 2.7-27 μm/s where 2.7 μm/s represents 1% of speed and 27 μm/s 100%. On Fig. S-1 (a) from top to bottom lines ablated with speed of 1, 5, 10, 20, 50 and 100% are shown. While Fig. S-1 (b and c) shows 5 μl droplets placed on laser irradiated circles with a diameter 1.5 mm and ablation speed of 1 and 100%, respectively).

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Electronic Supplementary Material

Micropatterning of Superhydrophobic Silicone Nanofilaments by Near-ultraviolet Nd:YAG

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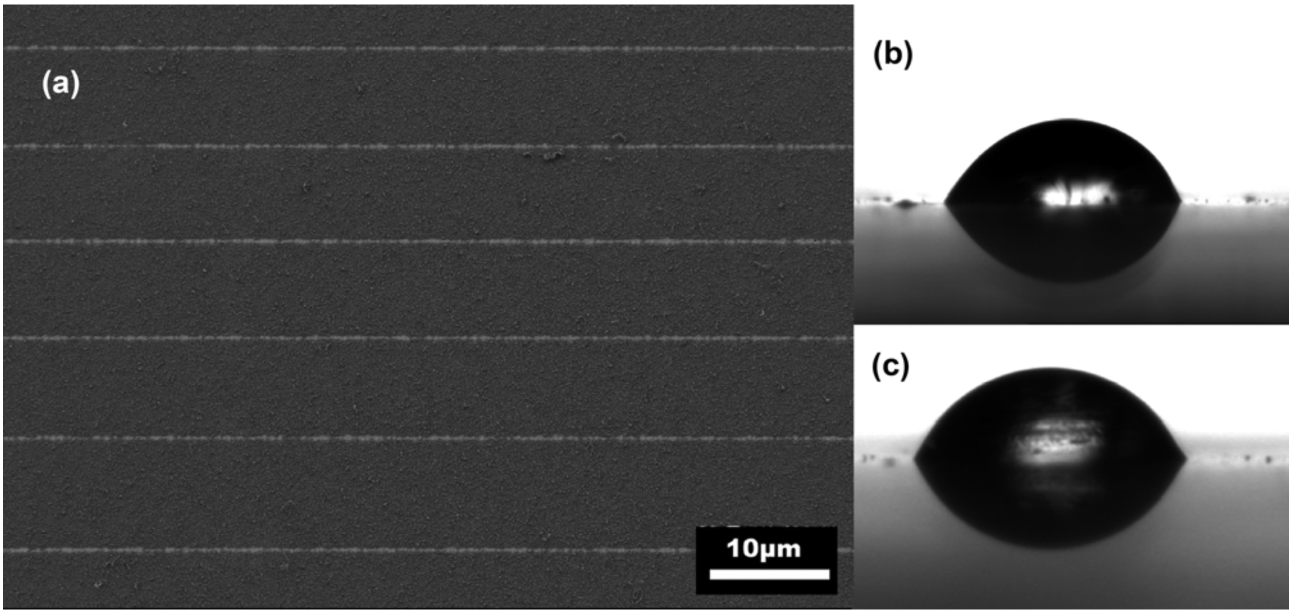

Figure S-1. Ablation speed versus wettability properties (a) line made by different ablation speed, from top to bottom speed is 1, 5, 10, 20, 50 and 100% respectively (b) droplet placed on irradiated circle; ablation speed was 100% (27 µm/s) and contact angle 61° (c) droplet placed on irradiated domain; ablation speed was 1% (2.7 µm/s) and contact angle 60°

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